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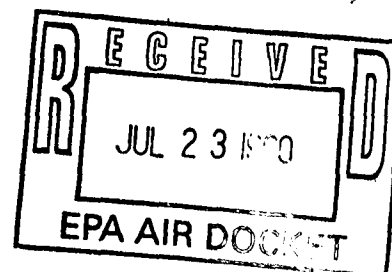


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A-90-16
IV-D-36

July 19, 1990

The Honorable William Reilly
Administrator
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460



Dear Mr. Reilly:

RE: Application for Fuel Additive Waiver by Ethyl Corporation Under Section 211(f)(4) of the Clean Air Act, Public Docket No. A-90-16

The Manufacturers of Emission Controls Association (MECA) is pleased to provide EPA with our comments regarding Ethyl Corporation's application for a waiver to market the fuel additive MMT. We are extremely concerned that the use of MMT in unleaded gasoline, even at the proposed concentration of 0.03125 (1/32nd) gram of manganese per gallon, will adversely affect catalyst performance and in turn impede the ability of motor vehicles to meet applicable emission standards -- particularly in light of the more stringent emission limits and durability requirements that will go into effect in the mid-1990s.

MECA is a non-profit association of companies which manufacture emission controls for motor vehicles -- most notably the catalytic converter. Our member companies have decades of experience in developing and applying catalyst technology for emission control purposes. We will limit our comments to impacts of manganese in gasoline on catalyst performance.

Over the years extensive research has been performed and reported detailing the adverse effects of manganese in gasoline on both the catalyst and vehicle emission performance, as well as demonstrating the mechanisms that impede catalyst performance. While most of this research was based on evaluations of higher concentrations of manganese than proposed in the Ethyl waiver, we believe that manganese even at a concentration of 1/32 grams per gallon (gpg) will adversely affect catalyst performance over time.

Catalyst experts from our member companies have identified five adverse effects from the combustion products of manganese: 1) coating of active catalyst sites; 2) plugging or clogging of the small flow channels of a monolith catalyst; 3) chemical reactions which reduce the catalyst surface area; 4) deterioration and reduced thermal durability of ceramic substrates; and 5) interference with improvements in precious metal/support interactions.

Coating of Active Catalyst Sites

MMT combustion products in the form of manganese oxide deposits on the catalyst surface will form a coating that will decrease catalyst performance. The manganese oxide deposits create resistance to mass transfer of the pollutant gases to the active catalyst sites. The thicker the coating, the more resistance to mass transfer that occurs. The effect of such coatings is that the time it takes the catalyst to light off during cold start increases and catalyst emission control performance is decreased in the hot condition.

A recent SAE Paper No. 890582 (copy attached) documented examples of manganese oxide coating of five to 20 microns in thickness. While this analysis evaluated catalysts equipped on vehicles which used gasoline with a higher concentration of manganese than proposed in the waiver application, our member companies' catalyst engineers believe the risk of coating still exists at a 1/32 concentration.

Plugging of Catalyst Substrate Channels

Manganese oxide deposits have been shown to completely clog small flow channels of a monolith catalyst. This phenomenon has been well documented at concentrations higher than the proposed levels in Ethyl's application. At a level of 1/32 gpg manganese, our member companies' engineers believe the mechanism of deposit probably will be lessened, but not eliminated.

Chemical Reaction Resulting in Reduced Catalyst Surface Area

Manganese oxides can react with the active catalyst surfaces to form spinel which causes the surface areas to collapse with a resulting loss in catalyst surface area. Specifically, manganese oxide (Mn_2O_3) will readily react with the washcoat alumina (Al_2O_3) at 900°C to form spinel. The alumina typically used in catalyst coatings have a high surface area. When spinel is formed, the surface area collapses resulting in changes to the preferred catalyst coating matrix containing the active catalyst sites. When manganese oxides are impregnated onto high surface area alumina washcoat, loss of surface area has been detected at 750C. As the amount of the manganese oxide increases in the catalyst, the spinel formation results in an increased loss of BET surface area.

Deterioration of Ceramic Substrate

If the manganese reaches the catalyst substrate in the form of manganese oxide, it can react with the cordierite used in ceramic monolith catalysts. This reaction can cause cordierite decomposition, as well as lowering the cordierite's melting point.

Research has shown that manganese oxide will react with cordierite in the temperature range of 800 to 1150°C for periods of one to 17 hours in a vacuum.¹ After 950°C/one hour (and presumably at the higher temperatures), the mix consisted of cordierite, Mn_2SiO_4 , and spinel. The spinel and cordierite could contain some manganese oxide. This result indicated that the manganese oxide caused enough cordierite decomposition to provide the quantity of SiO_2 required to form Mn_2SiO_4 (tephroite). One gram of MnO would destroy 0.42 grams of cordierite in this reaction. These new phases have higher thermal expansions and would raise the thermal expansion of the substrate.

Another problem identified by our member companies' ceramic engineers is a possible loss in refractoriness. Tephroite melts congruently at temperatures as low as 1347°C and probably reacts with cordierite and spinel to form eutectic melting at a considerably lower temperature.²

Finally, manganese cordierite melts incongruently at 1200°C. Consequently, the manganese oxide in solid solution in the cordierite could be expected to lower the melting point of the cordierite phase in the substrate and thereby reduce the refractoriness of the substrate.³

Interference with Improvements of Precious Metal/Support Interactions

Meeting more stringent standards and extended durability requirements will require improved catalyst performance. Catalyst manufacturers are devoting considerable attention to unique precious metal and support interactions with the objective of enhancing desirable interactions and minimizing undesirable interactions. Manganese oxide and salts are active materials and our catalyst engineers are concerned that accumulation of these materials on the washcoat will interfere with desirable improvements that are expected to result from current research efforts.

CONCLUSION

Ethyl Corporation has made a good faith effort to demonstrate that its additive will not adversely affect emission

control performance. Nevertheless, we believe, for the reasons discussed above, that serious questions remain concerning the adverse effects of manganese on catalyst performance even at a concentration of 1/32 gpg.

With standards soon to be tightened and durability requirements increased, catalyst manufacturers are engaged in extensive research and development efforts to improve catalyst performance to help insure that these new requirements are met. Introduction of any additive which could adversely affect catalyst performance would have serious consequences on efforts to meet these new emission control requirements.

Before EPA grants a waiver permitting the use of any additive containing manganese at any level, we believe substantially greater testing and evaluation is necessary. Such evaluations must include careful examination of catalysts (including chemical analysis) exposed to manganese oxides; back pressure tests alone are not adequate. Also, durability data needs to be significantly expanded to evaluate a variety of vehicle models/control systems under a full range of "real world" operating conditions.

We hope the information provided is helpful to EPA in reaching a decision on this important issue. If we can be of further assistance to you or your staff, please call me.

Sincerely,



Bruce I. Bertelsen
Executive Director

Attachment

cc: Public Docket No. A-90-16

Footnotes

1. G. Pourroy, J. L. Guille, and P. Poix, "Reactivity of Metal Oxides Cu_2O , MnO , CoO , NiO , CuO , and ZnO with Indialete," *Chem. of Materials*, 2, 101-105 (1990).
2. R. S. Roth, J. R. Dennis, and H. F. McMurdic, "Phase Diagrams for Ceramists," Vol. VI, 1987; Fig. #6411.
3. R. B. Snow, "Equilibrium Relationships on the Liquidus Surface in Part of the $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ System." *J. A. Cer. S.* 26(1) 11-20 (1943).